METASTABLE CLOSE-PACKED STRUCTURES IN SILVER-RICH BINARY ALLOYS WITH TIN, ANTIMONY AND SILICON

W. KLEMENT, JR.

APRIL 1963

A REPORT ON RESEARCH CONDUCTED UNDER CONTRACT FOR THE U.S. ATOMIC ENERGY COMMISSION AND THE OFFICE OF NAVAL RESEARCH

W. M. KECK LABORATORY OF ENGINEERING MATERIALS

CALIFORNIA INSTITUTE OF TECHNOLOGY

PASADENA

5 486300 7 NA 8 9

California Institute of Technology

W. M. Keck Laboratory of Engineering Materials

6

METASTABLE CLOSE-PACKED STRUCTURES IN SILVER-RICH BINARY ALLOYS WITH TIN, ANTIMONY AND SILICON

by

10

W. Klement, Jr.

16 NA

12 6p. 13 NA 14 17

~~Technical Report No~~. 14 submitted to:

U. S. Atomic Energy Commission Contract No. AT(04-3)-221 and

Office of Naval Research, Contract [redacted]. Nonr-220(30)

15

Approved by Pol Duwez
Professor of Engineering

11

Apr[redacted]63

1. INTRODUCTION

A recent study(1) of Ag-Ge alloys rapidly quenched from the melt showed that the solid solubility in face-centered-cubic (fcc) silver could be metastably extended to 13.0 ± 1.0 at. pct. Ge. This composition corresponds to an electron concentration of 1.39 ± 3, which is approximately the limit of primary solid solubility empirically established(2) for many Cu-, Ag- and Au- base alloys with the Group B elements. At least two factors detracted from the cogency of the Ag-Ge results; (i) the fcc solubility limit was determined from lattice parameters which vary only slightly with germanium content and were barely outside the range of experimental uncertainty and (ii) some hexagonal close-packed (hcp) structures were detected in conjunction with the fcc phases in the quenched alloys. The present investigation was undertaken in order to attempt to metastably extend the primary solid solubility limit in Ag-base binary alloys with Sn, Sb and Si by rapidly quenching these alloys from the melt.

2. EXPERIMENTAL PROCEDURE

Alloys were prepared from elements of purity greater than 99.9% by means of techniques fully described elsewhere(1)(3). The quenching procedures and details of the Debye-Scherrer x-ray measurements were much the same as previously(1)(3)(4). Weight losses in the alloy preparation were negligible; the reproducibility of the lattice spacings suggests that the compositions are within ± 0.2 at. pct.

3. RESULTS

Lattice parameters obtained for the Ag-Sn and Ag-Sb alloys are presented in Fig. 1, together with the results of Owen and Roberts[5]. Diffraction lines from hcp phases were also detected on the films; the relative visual intensities of the fcc (200) and hcp (10.2) lines were visually estimated as:

	(200)	(10.2)
11.1 at. pct. Sn;Ag	m	vvw
12.7	m	vw
12.9	m	vw
7.1 at. pct. Sb;Ag	m	vw
8.4	m	w
9.5	w	vw

For a quenched 13.6 at. pct. Sn;Ag alloy, the intensities were m for the (200) line and w for the (10.2), these being too much of the hcp phase to reliably obtain a lattice spacing for the fcc structure.

For these alloys, the lattice parameters vary linearly with composition up to ~8.0 at. pct. Sb and ~13.0 at pct. Sn, respectively. These compositions will be referred to as the metastable solid solubility limits and may be compared with the maximum equilibrium solid solubilities[6] of 7.2 at. pct. Sb. and 11.5 at. pct. Sn, respectively. The hcp phases, which were found together with the fcc phases, are believed to be of the same composition for those alloys of compositions less than the metastable solubility limits and this may be understood from a consideration of the solidification process.

It is necessary[3][4] to delineate the factors controlling both the nucleation and growth rates for the phases. For the present, rapidly

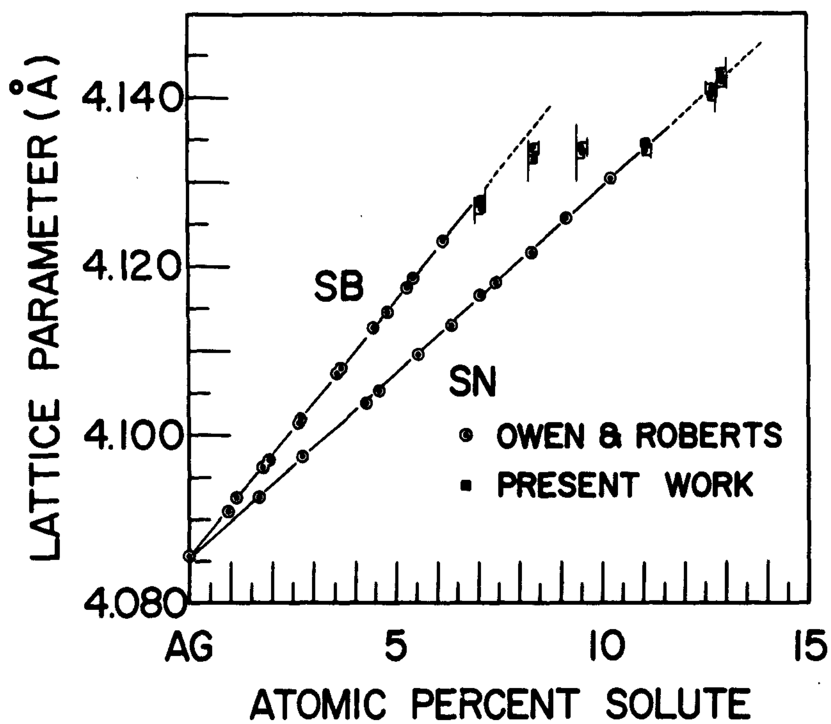

Fig. 1. Lattice Parameters of Silver-rich Solid Solutions with Sb and Sn.

quenched alloys, there is considerable undercooling of the melt and the growth rates of the solidifying phases are high. There should not be, however, much appreciable difference in growth rates between disordered fcc and hcp phases because of the similarity in packing. In nucleation, that phase with the lowest free energy will be favored. Since the difference in free energy between the fcc and hcp phases in the narrow two-phase equilibrium region is apparently small[7] for the Ag-Sn and Ag-Sb alloys, it is plausible to expect both phases in the rapidly solidified alloys -- in accord with the experiments. The amount of the hcp phase present increases with increasing solute concentration since a slight advantage in nucleation accrues. Both fcc and hcp phases are of the same composition until the metastable solubility limit is approached -- it is then not possible to nucleate a fcc phase of greater solute concentration, probably because of an abrupt increase in free energy. A rapid increase in free energy at an electron concentration, $\lesssim 1.4$ has generally been considered to occur in a similar way for these Cu-, Ag- and Au- base alloys, although the mechanisms remain obscure[2].

Equally obscure is an explanation for the limited metastable solid solubility of antimony in silver, compared to germanium[1] and tin. Proceeding from the above arguments, it may be that an abrupt increase in free energy occurs at a lower electron concentration for the Ag-Sb alloys. Concomitant with the decreasing difference in free energy between the fcc and hcp phases near the solubility limit, there should be a sizeable decrease in stacking fault energy. This is found for Ag-Sn alloys[8] but not, apparently, for the Ag-Sb alloys[8]. Because of the similar behavior of the Ag-Sn and Ag-Ge alloys in these rapid quenching experiments, it is suggested that the stacking fault energy for the fcc solid solutions decreases rapidly with increasing solute concentration for the latter alloys also.

At equilibrium, the Ag-Si and Ag-Ge systems are homologous[6]; the primary solid solubility of silicon in silver is, however, apparently quite limited. Despite much effort with quenched samples of several compositions, it has not been possible to obtain lattice spacings which are sufficiently critical to establish either the variation of lattice spacing with solute content or the limit of metastable solid solubility for the Ag-Si alloys. Previous work[9] on these alloys indicates little solid solubility or variation in lattice parameter. The Si (111) diffraction line was not detected in alloy containing less than 16 at. pct. Si, due presumably to the difference in scattering power. For alloys in the range 10-25 at. pct. Si, faint low angle lines were detected and could be indexed as the (10.0), (00.2) and (10.1) reflections of an hcp structure with $\underline{a} = 2.87 \pm 3$, $\underline{c} = 4.52 \pm 3$ Å, $c/a = 1.57 \pm 2$. In contrast to Ag-Ge[1], there was no range of composition in which the hcp phase predominated at room temperature. The 16 at. pct. Si alloy was quenched to, and examined at, liquid nitrogen temperatures but no predominant hcp phase was found.

REFERENCES

1. W. Klement, J. Inst. Met., 90, 27 (1961).
2. T. B. Massalski and H. W. King, Prog. Mat. Sci., 10, 1 (1961).
3. W. Klement, Ph. D. Thesis, California Institute of Technology (1962)
4. W. Klement, Canad. J. Phys., 40, 1397 (1962).
5. E. A. Owen and E. W. Roberts, Phil. Mag., 27, 294 (1939).
6. M. Hansen and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York (1958).
7. R. Hultgren, et. al., Selected Values for the Thermodynamic Properties of Metals and Alloys, University of California, Berkeley, unpublished.
8. C. S. Barrett, Imperfections in Nearly Perfect Crystals, Wiley, New York (1952).
9. W. B. Pearson, Handbook of the Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, New York (1958).

DISTRIBUTION LIST FOR CONTRACT Nonr 220(30)

A

AGENCY	NUMBER OF COPIES
Chief of Naval Research Department of the Navy Washington 25, D. C. Attention: Code 423	2
Commanding Officer Office of Naval Research Branch Office 346 Broadway New York 13, New York	1
Commanding Officer Office of Naval Research Branch Office 495 Summer Street Boston 10, Massachusetts	1
Commanding Officer Office of Naval Research Branch Office 86 E. Randolph Street Chicago 1, Illinois	1
Commanding Officer Office of Naval Research Branch Office 1030 E. Green Street Pasadena 1, California	1
Commanding Officer Office of Naval Research Branch Office 1000 Geary Street San Francisco 9, California	1
Assistant Naval Attache for Research Office of Naval Research Branch Office, London Navy 100, Box 39 F.P.O., N.Y., N.Y.	5
Director U. S. Naval Research Laboratory Washington 25, D. C. Attention: Technical Information Officer, Code 2000	6
: Code 2020	1
: Code 6200	1
: Code 6300	2
: Code 6100	1

AGENCY	NUMBER OF COPIES
Chief, Bureau of Naval Weapons Department of the Navy Washington 25, D. C. Attention: Code RRMA	1
: Code RREN-6	1
Commanding Officer U. S. Naval Air Material Center Philadelphia, Pennsylvania Attention: Aeronautical Materials Laboratory	1
Chief, Bureau of Yards and Docks Department of the Navy Washington 25, D. C. Attention: Research and Standards Division	1
Commanding Officer U. S. Naval Ordnance Laboratory White Oaks, Maryland	1
Commanding Officer U. S. Naval Proving Ground Dahlgren, Virginia Attention: Laboratory Division	1
Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attention: Code 315	1
: Code 335	1
: Code 341	1
: Code 350	1
: Code 634	1
Commanding Officer U. S. Naval Engineering Experiment Station Annapolis, Maryland Attention: Metals Laboratory	1
Materials Laboratory New York Naval Shipyard Brooklyn 1, New York Attention: Code 907	1

AGENCY	NUMBER OF COPIES
Commanding Officer David Taylor Model Basin Washington 7, D. C.	1
Post Graduate School U. S. Naval Academy Monterey, California Attention: Department of Metallurgy	1
Office of Technical Services Department of Commerce Washington 25, D. C.	1
Commanding Officer U. S. Naval Ordnance Test Station Inyokern, California	1
Armed Services Technical Information Agency (ASTIA) Documents Service Center Arlington Hall Station Arlington, Va.	5
Commanding Officer Watertown Arsenal Watertown, Massachusetts Attention: Ordnance Materials Research Office	1
: Laboratory Division	1
Commanding Officer Office of Ordnance Research Box CM, Duke Station Duke University Durham, North Carolina Attention: Metallurgy Division	1
Commander Wright Air Development Center Wright-Patterson Air Force Base Dayton, Ohio Attention:	
: Aeronautical Research Lab. (WCRRL)	1
: Materials Laboratory (WCRTL)	1

AGENCY	NUMBER OF COPIES
U. S. Air Force ARDC	1
Office of Scientific Research	
Washington 25, D. C.	
Attention: Solid State Division (SRQB)	
National Bureau of Standards	
Washington 25, D. C.	
Attention: Metallurgy Division	1
: Mineral Products Division	1
National Aeronautics Space Administration	1
Lewis Flight Propulsion Laboratory	
Cleveland, Ohio	
Attention: Materials and Thermodynamics Division	
U. S. Atomic Energy Commission	1
Washington 25, D. C.	
Attention: Technical Library	
U. S. Atomic Energy Commission	
Washington 25, D. C.	
Attention: Metals and Materials Branch Division of Research	1
: Eng. Develop. Branch Division of Reactor Develop.	1
Argonne National Laboratory	1
P. O. Box 299	
Lemont, Illinois	
Attention: H. D. Young, Librarian	
Brookhaven National Laboratory	1
Technical Information Division	
Upton, Long Island, New York	
Attention: Research Library	
Union Carbide Nuclear Co.	
Oak Ridge National Laboratory	
P. O. Box P	
Oak Ridge, Tennessee	
Attention: Metallurgy Division	1
: Solid State Physics Division	1
: Laboratory Records Dept.	1

AGENCY	NUMBER OF COPIES
Los Alamos Scientific Laboratory P. O. Box 1663 Los Alamos, New Mexico Attention: Report Librarian	1
General Electric Company P. O. Box 100 Richland, Washington Attention: Technical Information Division	1
Iowa State College P. O. Box 14A, Station A Ames, Iowa Attention: F. H. Spedding	1
Knolls Atomic Power Laboratory P. O. Box 1072 Schenectady, New York Attention: Document Librarian	1
U. S. Atomic Energy Commission New York Operations Office 70 Columbus Avenue New York 23, New York Attention: Document Custodian	1
Sandia Corporation Sandia Base Albuquerque, New Mexico Attention: Library	1
U. S. Atomic Energy Commission Technical Information Service Extension P. O. Box 62 Oak Ridge, Tennessee Attention: Reference Branch	1
University of California Radiation Laboratory Information Division Room 128, Building 50 Berkeley, California Attention: R. K. Wakerling	1
Bettis Plant U. S. Atomic Energy Commission Bettis Field P. O. Box 1468 Pittsburgh 30, Pennsylvania Attention: Mrs. Virginia Sternberg, Librarian	1

AGENCY	NUMBER OF COPIES
Commanding Officer and Director U. S. Naval Civil Engineering Laboratory Port Hueneme, California	1
Commanding Officer U. S. Naval Ordnance Underwater Station Newport, Rhode Island	1
U. S. Bureau of Mines Washington 25, D. C. Attention: Mr. J. B. Rosenbaum, Chief Metallurgist	1
Defense Metals Information Center Battelle Memorial Institute 505 King Avenue Columbus, Ohio	2
Solid State Devices Branch Evans Signal Laboratory U. S. Army Signal Engineering Laboratories c/o Senior Navy Liaison Officer U S. Navy Electronic Office Fort Monmouth, New Jersey	1
U. S. Bureau of Mines P. O. Drawer B Boulder City, Nevada Attention: Electro-Metallurgical Div.	1
Commanding General U. S. Army Ordnance Arsenal, Frankford Philadelphia 37, Pennsylvania Attention: Mr. Harold Markus ORDBA-1320, 64-4	1
Picatinny Arsenal Box 31 Dover, New Jersey Attention: Lt. Hecht	1

AGENCY	NUMBER OF COPIES
Professor M. Cohen Department of Metallurgy Massachusetts Institute of Technology Cambridge 39, Massachusetts	1
Professor B. L. Averbach Department of Metallurgy Massachusetts Institute of Technology Cambridge 39, Massachusetts	1
Professor G. M. Pound Department of Metallurgical Engineering Carnegie Institute of Technology Pittsburgh 13, Pennsylvania	1
Professor B. E. Warren Department of Metallurgy Massachusetts Institute of Technology Cambridge 39, Massachusetts	1
Professor R. F. Hehemann Department of Metallurgical Engineering Case Institute of Technology Cleveland, Ohio	1
Professor G. C. Kuczynski Department of Metallurgy University of Notre Dame Notre Dame, Indiana	1
Professor J. M. Sivertsen Department of Metallurgy University of Minnesota Minneapolis, Minnesota	1
Professor V. G. Macres Department of Metallurgical Engineering Stanford University Stanford, California	1
Professor L. V. Azaroff Department of Metallurgical Engineering Illinois Institute of Technology Chicago 16, Illinois	1
Professor F. Seitz Department of Physics University of Illinois Urbana, Illinois	1

H

AGENCY	NUMBER OF COPIES
Professor T. A. Read Department of Mining & Met. Engrg. University of Illinois Urbana, Illinois	1
Professor R. Smoluchowski Department of Mechanical Engineering Princeton University Princeton, New Jersey	1
Professor H. Brooks Dean of Graduate School of Applied Science Harvard University Cambridge, Massachusetts	1
Professor C. E. Birchenall Princeton University Princeton, New Jersey	1
Professor W. E. Wallace Department of Chemistry University of Pittsburgh Pittsburgh, Pennsylvania	1
Professor E. R. Parker Division of Mineral Technology University of California Berkeley 4, California	1
Professor L. G. Parratt Department of Physics Cornell University Ithaca, New York	1
Professor P. A. Beck Department of Mining and Metallurgy University of Illinois Urbana, Illinois	1
Professor P. Gordon Department of Metallurgical Engineering Illinois Institute of Technology Chicago 16, Illinois	1
Professor J. T. Norton Massachusetts Institute of Technology Department of Metallurgy Cambridge 39, Massachusetts	1

AGENCY	NUMBER OF COPIES
Professor M. E. Nicholson Department of Metallurgy University of Minnesota Minneapolis 14, Minnesota	1
Professor J. W. Spretnak Department of Metallurgy Ohio State University Columbus, Ohio	1
Professor C. H. Shaw Department of Physics Ohio State University Columbus, Ohio	1
Professor F. R. Brotzen Department of Mechanical Engineering The Rice Institute Houston, Texas	1
Professor S. Weissman Materials Research Laboratory Rutgers University New Brunswick, New Jersey	1